

BAND SPECTRUM OF CrF MOLECULE

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(Received for publication, July, 16, 1951)

Plates : XIX A-B

ABSTRACT. Two band systems (I and II) attributable to CrF molecule were obtained in emission in a heavy current discharge in the regions $\lambda\lambda$ 4230—4470 A.U. and $\lambda\lambda$ 3830—4050 A.U. respectively. System I was interpreted as due to the electronic transition ${}^6\Pi \rightarrow {}^6\Sigma$ and System II as due to a transition ${}^6\Sigma \rightarrow {}^6\Sigma$ with a common lower state. The ω_e value is observed to be approximately 520 cm^{-1} .

INTRODUCTION

The band spectrum of CrCl molecule was studied by one of us (V. R. Rao) and K. R. Rao (1949) and shown to be due to a transition ${}^6\Pi \rightarrow {}^6\Sigma$. The spectrum of CrBr was also investigated by V. R. Rao (1949). It was felt that if the spectrum of CrF molecule is also studied, a comparison between the characteristics of the spectra of different halides of chromium can be made. The transitions might be expected to be similar to that in CrCl. The results of our study of the CrF spectra are described below.

EXPERIMENTAL

The substance chromium fluoride supplied by Thomas Tyrer and Co. London, was used in these investigations. The experimental technique was the same as used in the investigations on CrCl and CrBr (Loc. cit.). A characteristic discharge of bright yellow colour is obtained at 2000 V. and 0.8 amperes. Photographs are taken on Ilford Sclochrome plates on Fuess instrument with a dispersion of 20 Å/mm. in the region λ 4400 A.U. Exposures of about half an hour were required to record the spectrum. As the intensity of the bands is very low, they could not be obtained on a higher dispersion instrument.

DESCRIPTION OF THE SPECTRUM

When the vapour of CrF was excited by the generator discharge bands were obtained in the region $\lambda\lambda$ 4573—3800 A.U. The region is also overlaid with strong atomic lines. They appear in two different groups. One of them, i.e. the stronger one lies in the region $\lambda\lambda$ 4230—4470 A.U. The second group

(see figure 2 in Plate XIX B) which consists of four weak groups, lies in the region $\lambda\lambda$ 3830—4050 A.U. This appears to have a less complicated structure than the first group.

ANALYSIS

From the intensity distribution of the band groups and a comparison with allied halides, the bands could be divided into two system: (1) in the region $\lambda\lambda$ 4467—4198 A.U. and (2) in the region $\lambda\lambda$ 3993—3840 A.U. The long wavelength system, hereafter referred to as System I, is of a very complex structure as in TiCl, MnCl and CrCl, etc. Possibly this is due to the transition ${}^6\Pi \rightarrow {}^6\Sigma$. System II, the one on the shorter wavelength side appears comparatively simpler and may be due to the transition ${}^6\Sigma \rightarrow {}^6\Sigma$. The lower Σ state is possibly common to both,

The three states ${}^6\Sigma$, ${}^6\Pi$ and ${}^6\Sigma$ may be derived as follows. The chromium atom with 6 effective electrons and the fluorine atom with 5 effective electrons have the following electron configurations.

Cr: $1s^2 2s^2 2p^6 3s^2 3p^3 3d^5$ giving a as ground term,

F: $1s^2 2s^2 2p^5$ giving a as ground term.

In the molecule CrF the configuration

$$\sigma^2 \pi^4, \sigma \pi^2 \delta^2$$

gives a ${}^6\Sigma$ term as in CrCl. The following configurations

$$\sigma^2 \pi^4, \pi^2 \delta^2 \pi \rightarrow {}^6\Pi \quad \text{and}$$

$$\sigma \pi^4 \pi, \pi^2 \delta^2 \pi \rightarrow {}^6\Sigma$$

involving single and double electron excitation, give the two upper states noted against them. Transitions from these to the lower state ${}^6\Sigma$ give two band systems with ${}^6\Sigma \rightarrow {}^6\Sigma$ lying to the short wavelength side of ${}^6\Pi \rightarrow {}^6\Sigma$. The former has a simple structure as both states are Σ 's. The latter has a more complicated structure involving six multiplets of ${}^6\Pi$ state and some rotational branches (vide CrCl).

It is necessary now to determine the forms of rotational heads to be expected in these bands. The formulae for individual forms of rotational heads are given in the paper on CrCl (Loc. cit). Following the steps given there, we find in red-degraded bands in which $B'' > B'$, we can expect only the R, S, T and Q forms to form the heads. The K_h values are as follows.

Form	Q	R	S	T
K_h	0	$\frac{3B' - B''}{2(B' - B'')}$	$\frac{5B' - B''}{2(B' - B'')}$	$\frac{7B' - B''}{2(B' - B'')}$

The possible theoretical transitions for this type of red-degraded bands have not been worked out earlier (the CrCl bands are violet degraded). The list of theoretical transitions is given below. Each of the letters A to U represents

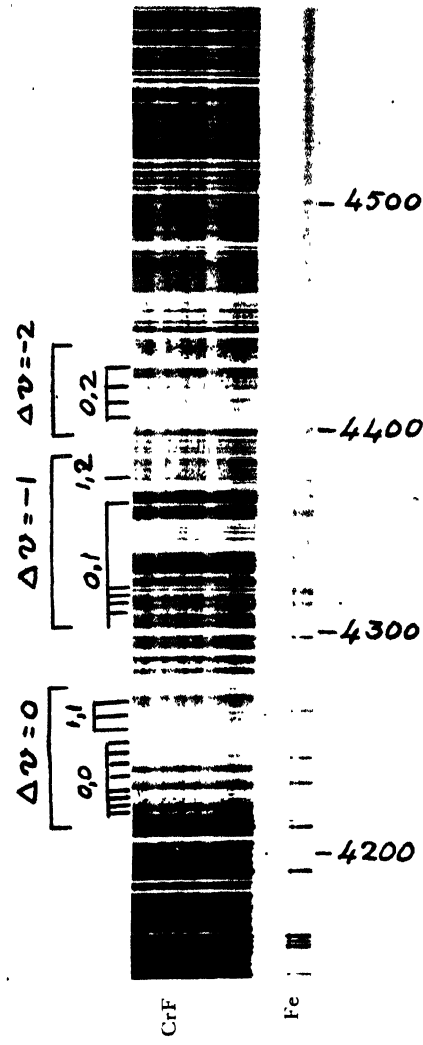


Fig. 1
Band spectrum of CrF System I

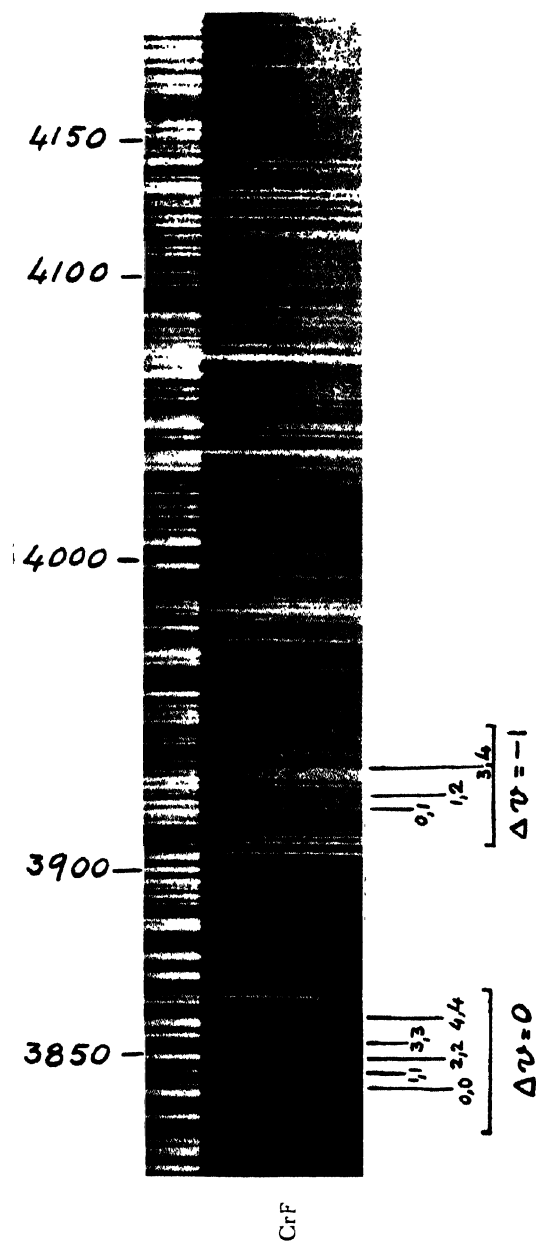


Fig. 2
Band spectrum of CrF. System II

the various bands that are not resolved and so found as one band. Thus corresponding to each $v' v''$ transition we can expect 21 bands, some of them being multiplet components, and the others various forms of the rotational heads. Table I gives for any particular $v' v''$ transition the positions of the various bands in terms of the symbols A to U. A structure like this can be held responsible for the very complicated appearance of the band system. The direction of the arrow (Table II) indicates the increasing frequency.

TABLE I
List of theoretical transitions

$\Delta I =$	1	0	-1	Symbol
	TR_{12}	TQ_1		U
	SR_{13}	SQ_{12}	SP_1	T
	R_{14}	RQ_{13}	RP_{12}	S
	QR_{15}	Q_{14}	QP_{13}	R
	TR_{23}	TQ_2	TP_{21}	Q
	SR_{24}	SQ_{23}	SP_2	P
	R_{25}	RQ_{24}	RP_{23}	O
	QR_{26}	Q_{25}	QP_{24}	N
	TR_{34}	TQ_3	TP_{32}	M
	SR_{35}	SQ_{34}	SP_3	L
	R_{36}	RQ_{35}	RP_{34}	K
		Q_{36}	QP_{35}	J
	TR_{45}	TQ_4	TP_{43}	I
	SR_{46}	SQ_{45}	SP_4	H
		RQ_{46}	RP_{45}	G
			QP_{46}	F
			TP_{54}	E
	TR_{56}	TQ_5	SP_5	D
		SQ_{56}	RP_{56}	C
		TQ_6	TP_{65}	B
			SP_6	A

TABLE II
Multiplets

Form	F_6		F_4			F_1	
T	\downarrow	B	E	\rightarrow I	M	Q	U
S		A	D	II	L	P	T
R	\uparrow	—	C	G	K	O	S
Q		—	—	F	J	N	R

For an analysis of this type of bands we should have an approximate idea of the lower state vibrational frequencies and the multiplet separation factors. Table III gives a collection of the ω_e'' values for allied halides.

TABLE III
Lower state frequencies, ω_e'' in some halides of the transition group of elements.

	Ti	Cr	Mn	Fe	Co	Ni
Fluoride	—	510	612	—	—	740
Chl ride	455	292	385	405	401	416
Bromide	—	—	290	—	305	312

It would be seen that the chlorides of the various elements have their ω_e'' values ranging between 300 cm^{-1} and 450 cm^{-1} increasing from chromium to nickel. Similar features exist in fluorides and bromides as well, as far as they are investigated. We can therefore expect that in chromium fluoride the ω_e'' may lie in the region $500\text{--}600\text{ cm}^{-1}$. The multiplet separation factor (A) in chromium chloride was found to be nearly 46 cm^{-1} while in chromium bromide it was suggested that it might be about 52 cm^{-1} . It is known that this A factor should decrease from a bromide to a chloride. So in chromium fluoride it might be between 30 cm^{-1} and 40 cm^{-1} . We expect six multiplet components in chromium fluoride corresponding to the ^6II level. If the above orders of magnitude are correct then $6 \times 35 = 210\text{ cm}^{-1}$ or a maximum of 300 cm^{-1} appears to be the spread of the multiplet. This is less than the value of ω_e'' predicted earlier. So an overlap of the vibrational structure and multiplet structure need not be expected.

During our attempts of analysis the presence of strong lines in the whole region of the spectrum proved a great handicap. They appear to have obscured quite a few important bands. Besides, their presence in the immediate proximity of a band gives anomalous impressions about relative

intensities. Under the circumstances the assignments given in Table IV for System I and Table IV for System II appear to be reasonable. The features of this analysis are described below.

SYSTEM II

In Table IV about 19 bands that could be definitely distinguished from lines are given. 8 bands could be analysed as forming two sequences ($\Delta v = 0$ and -1) as shown in the Deslander's scheme (Table V). The $\Delta v = +1$ sequence was in the region below 3840 A.U. and the appearance of the bands in this region is not very definite. Hence we might conclude that the sequence is very weak in intensity and does not manifest itself. This feature seems to be shared by System I as well as will be pointed out later. The ground state differences are of the order of 525 cm^{-1} while the upper state differences

TABLE IV
Catalogue of CrF band-heads. System II

Wavelength A.U.	Wavenumber cm^{-1}	Intensity	$v' v''$
3993.5	25034	1	
3987.4	25072	2	
3984.4	25091	7	
3978.8	25126	1	
3975.4	25148	2	
3969.8	25183	1	
3959.5	25249	0	
3938.5	25383	3	
3933.8	25414	6	3,4
3925.3	25469	0	1,2
3921.6	25493	5	0,1
3899.2	25639	2	
3895.8	25661	1	
3882.3	25751	1	
3876.9	25787	1	
3860.2	25898	3	4,4
3854.4	25937	2	3,3
3850.2	25965	3	2,2
3846.6	25990	2	1,1
3841.7	26023	6	0,0

TABLE V

Deslander's scheme

v''	v'		1		2	3		4
0	0	530	25493 (5) 497					
1			25990 (2)	521	25469 (0) 496			
2					25965 (3)			
3						25937 (2)	523	25414 (6) 484
4								25898 (3)

appear to be about 490 cm^{-1} . The development of the sequences instead of progressions is a comparison to the similar case in the corresponding system in TiCl (Rao, 1949)

From the spectrogram (figure 2) it appears that $\Delta v = -1$ sequence looks stronger than the $\Delta v = 0$ sequence. Part of this intensity may be attributed to the strong atomic lines present in this region. Besides, no progress could be achieved with our attempts to locate at the (0,0) band in this apparently more intense group; a $\Delta v = -1$ sequence could not be located consistent with the red-degradation of the bands ($\omega_e' < \omega_e''$). The analysis presented here is the only one that satisfied all the above requirements, besides those demanded by an analysis of System I as well.

This following approximate values may be assigned to the various vibrational constants and ν_e for this system.

$$\begin{aligned} \nu_e &= 26041\text{ cm}^{-1} & \omega_e' &= 499.9\text{ cm}^{-1} & x_e' \omega_e' &= 1.9\text{ cm}^{-1} \\ & & \omega_e'' &= 535.6\text{ cm}^{-1} & x_e'' \omega_e'' &= 2.78\text{ cm}^{-1} \end{aligned}$$

This simple band system may be attributed to the transition ${}^6\Sigma \rightarrow {}^6\Sigma$.

SYSTEM I

This system occurs in three groups in the region $\lambda\lambda\ 4199-4467\text{ A.U.}$ of which the one on the short wavelength side is the strongest. As a starting point in the analysis regularities in these band groups of the order of 35 cm^{-1} (as predicted earlier) have been attempted and sorted out in each of these groups. The frequency shifts vary between 27 cm^{-1} and 37 cm^{-1} and may be considered as the multiplet separations with a mean value of 32 cm^{-1} . Connected with the above bands are also some additional bands

with frequency shifts of about 18 cm^{-1} . This may be considered as the shift between the various rotational forms of the same multiplet component. The corresponding value in CrCl varies between 5 and 17 cm^{-1} with increasing shifts from *Q* to *P*, *P* to *O* and *O* to *N* forms. If we expect in CrF a similar increasing tendency with higher forms (*Q* to *T*), we might consider the comparatively high value of 18 cm^{-1} as the separation between *S* and *T* forms. Bands with smaller separations have not been found. They are either submerged by atomic lines or not resolved.

TABLE VI
Catalogue of CrF band-heads. System I

Wavelength A.U.	Wavenumber cm^{-1}	Intensity	$v' v''$	Symbol
4467.2	22379	3		
4462.7	22402	3		
4459.6	22417	2		
4455.3	22439	2		
4453.2	22450	2		
4431.1	22561	5	0,2	E
4423.1	22602	1	0,2	I
4411.3	22563	1	0,2	Q
4404.5	22698	1	0,2	U
4401.0	22716	5		
4398.5	22729	1		
4388.5	22781	1		
4379.1	22829	1		
4373.1	22861	0		
4368.5	22885	4	1,2	E
4340.3	23033	2	0,1	B
4323.0	23126	1	0,1	M
4316.0	23163	1	0,1	Q
4313.6	23176	1	0,1	T
4309.8	23196	1	0,1	U
4305.1	23222	1		E
4272.2	23401	2	1,1	I
4264.0	23446	3	1,1	M
4258.2	23478	2	1,1	A
4251.6	23514	1	0,0	D
4244.6	23553	1	0,0	E
4241.5	23570	0	0,0	I
4235.3	23605	8	0,0	M
4229.6	23636	6	0,0	P
4227.4	23649	2	0,0	Q
4224.3	23666	2	0,0	U
4219.4	23693	2	0,0	
4158.8	23810	1		

Accepting these groups and taking the differences between corresponding bands in the groups $\lambda\lambda 4219-4305 \text{ A.U.}$ and $\lambda\lambda 4309-4373 \text{ A.U.}$, we obtain an average shift of 500 cm^{-1} . This is of the same order of magnitude as the value we obtain for the first lower state difference in System II. Thus our expectation that both the systems must have a common lower state is justified. The first group therefore is the $\Delta v=0$ group and the second one is the $\Delta v=-1$ group. In the third group between

λ 4400 A.U. and λ 4467 A.U., a few more bands could be identified as belonging to $\Delta v = -2$ group. Table VI contains all these bands with their assignments. For the meaning of the symbols E, I, Q, U etc. reference may be made to Table II. It would be seen from this table that only a few bands could be identified as belonging to (1,1) group in the $\Delta v = 0$ group. Such fragmentary identifications for higher members of the sequence are not uncommon in these complex spectra. The $\Delta v = +1$ group is not definitely observed in the spectrum. The nature of a few very weak bands in the possible region is doubtful. This feature is shared by System II as well. The upper state vibrational frequency could therefore be fixed up at about 338 cm^{-1} . This is smaller than the lower state frequency and consistent with the red-degradation of the bands. The Deslander scheme of intervals in (0,0) group is given in Table VII

TABLE VII
Intervals in the (0,0) group

v''												
	ΔK	${}^6\Pi$		${}^6\Pi$		${}^6\Pi$		${}^6\Pi$		${}^6\Pi$		${}^6\Pi$
v'	T	B		E	35	I	31	M	30	Q	27	U
				17				17				
	S	A	39	D		H		L		P		T
	R	—		C		G		K		O		S
	Q	—		—		F		J		N		R

This analysis may be considered to satisfy the requirements of the transition ${}^6\Pi \rightarrow {}^6\Sigma$. The coupling constant has a value of about 35 cm^{-1} , with $\omega_e' \simeq 338 \text{ cm}^{-1}$ and $\omega_e'' \simeq 510 \text{ cm}^{-1}$.

ACKNOWLEDGMENTS

Our thanks are due to Prof. K. R. Rao, for his kind interest in the work.

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